Carbon Dioxide Activation Center 2023 - HIGHLIGHTS

About the Center

The Carbon Dioxide Activation Center (CADIAC) was established in 2015 at Aarhus University. Currently, the research center is led by Prof. Troels Skrydstrup, which includes three local research teams. The center also encompasses one of the leading research teams devoted to catalysis in Europe located at the Leibniz Institute of Catalysis in Rostock. The goals of the research center are two-fold: 1) to identify new catalytic technologies for the transformation of carbon dioxide to high-value chemicals of industrial importance, and 2) to develop new carbon isotope labeling strategies starting from CO_2 specifically directed to pharmaceutical development programs. The highlights of the published work from CADIAC for the year 2022 and start of 2023 are described below. As in the other years of the Center's existence, once again the CADIAC publication record has been excellent with publications in *JACS Au*, *Angewandte Chemie International Edition, ACS Catalysis, Nature Communications and Nature Synthesis* representing some of the top scientific journals related to Chemistry. (See discussion on page 2 of the report). CADIAC has also paved the way for the establishment of a new center on CO_2 capture and conversion in the beginning of 2022, being funded by the Novo Nordisk Foundation. Such parallel research activities provide substantial support to our CADIAC activities to the development of key solutions for the creation of a sustainable society.

Playing with Product Selectivity with Manganese Electrocatalyst for CO_2 Conversion

To date, manganese-based bipyridine complexes as molecular electrocatalysts have displayed some of the most interesting activities for CO_2 reduction. CADIAC scientists at Aarhus University in collaboration with chemists at the University of Oslo have recently published in *ACS Catalysis* on the product selectivity switch in the electroconversion of CO_2 to either carbon monoxide or formic acid to the synthesis of hydrogen. This was observed when the two ends of the amine containing appendages of the bipyridine ligand were tied up as a macrocycle. The study included both synthesis, electrochemical investigations and DFT calculations to understand the chemistry observed. These results reveal how product selectivity can be modulated by ligand design in Mn-based catalysts, providing atomistic details that can be leveraged in the development of a fully selective system.

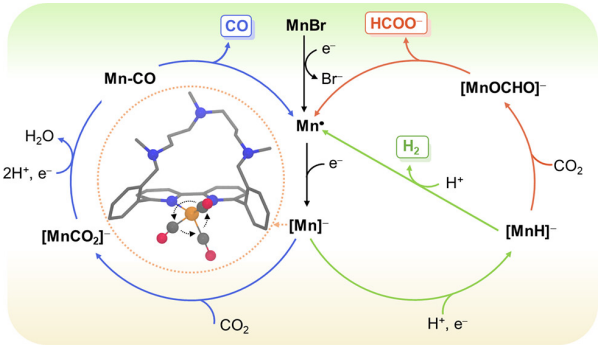

Figure 1: A catalytic cycle explaining the product selectivity of manganese-based bipyridine complexes displaying locked amines.

Catalytic Carbonylations Applying Carbon Dioxide

A team of CADIAC chemists in Rostock reported in *Nature Communications* an interesting two-step cascade process comprising of the chemical reduction of CO_2 to carbon monoxide, which is then directly applied for important industrial chemical transformations. A novel heterogeneous copper 10Cu@SiO_2-PHM catalyst was found to exhibit high selectivity (≥98%) and decent conversion (27%) in generating CO from the reduction of CO_2 with H_2. The generated CO was directly utilized without further purification in various industrial carbonylation reactions including hydroformylations, alkoxycarbonylations, and aminocarbonylations. Particularly noteworthy, various aldehydes, (unsaturated) esters and amides were obtained in high yields and chemo-/regioselectivities at low temperature under ambient pressure. This approach is of interest for continuous syntheses to produce building blocks on reasonable scale utilizing CO_2.

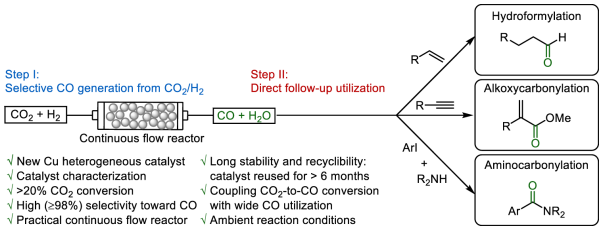

Figure 2: Selective Cu-catalyzed generation of carbon monoxide from CO_2 and follow-up utilization in carbonylation reactions.

Rapid Access to Carbon-Isotope-Labeled Alkyl and Aryl Carboxylates Applying Organometallic Complexes

In collaboration with researchers from AstraZeneca in Gothenburg, Sweden, CADIAC chemists at Aarhus University have published a method in *JACS Au* for the synthesis of carbon-13 and carbon-14 labeled alkyl and aryl carboxylates. This was achieved utilizing the combination of various aryl and alkyl boronic acids with an easily accessible air stable palladium carboxylate complex whereby the origin of the isotope label is from CO_2. The method is characterized by its operational simplicity, mild conditions, and broad substrate scope, including pharmaceutically relevant compounds. The procedure was further extended to a carbon isotope replacement strategy, involving a decarbonylative borylation reaction directly from carboxylic acids. This extension provides access to carbon-isotope-labeled compounds in only three steps from the unlabeled pharmaceutical. These results can have implications for drug discovery programs where it is ideal to install the isotope-label as late as possible in the synthesis.

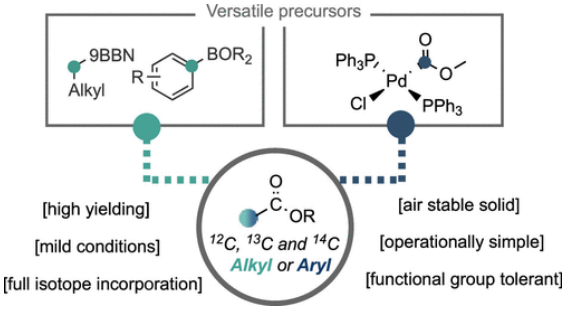

Figure 3: Application of palladacarboxylates as a carboxylation source for carbon isotope labeling with aryl boronic acids.

References

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[2] Sang, R.; Hu, Y.; Razzaq, R.; Mollaert, G.; Atia, H.; Bentrup, U.; Sharif, M.; Neumann, H.; Junge, H.; Jackstell, R.; Maes, B. U. W.; Beller, M. A practical concept for catalytic carbonylations using carbon dioxide. *Nat. Commun.* **2022**, *13*, article. no. 4432.

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